

FINE PARTICLE AND PRECURSOR EMISSIONS FROM POWER, OIL AND GAS INDUSTRY COMBUSTION SOURCES

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Summary

The U.S. EPA's new fine particle ambient air quality standards for fine particles (PM_{2.5}) are scheduled for review in 2002. At the same time, EPA is expected to begin designating non-attainment areas based on ambient air monitoring data and states implementation plans for achieving the national standards will follow in three years. To understand the contribution of stationary sources to ambient PM_{2.5}, the mass and chemical composition of source PM_{2.5} emissions is needed. Emissions data for gaseous PM_{2.5} precursors – e.g., ammonia, SO₂, NO_x, organics, etc. – also are needed. Once a complete inventory of chemically-speciated source emissions is established, source apportionment techniques can be used to identify significant contributors to PM_{2.5} and to evaluate the effectiveness of source control strategies. The chemical composition (e.g., elemental, organics) of source emissions is especially valuable information for “fingerprinting” ambient PM_{2.5} sources. New methods are needed to develop combustion source emission factors and chemical speciation profiles for primary particulate matter and secondary particle precursors to help formulate state implementation plans.

In January, 2001 the U.S. Department of Energy's National Petroleum Technology Office (DOE NPTO), the Gas Technology Institute (GTI), the American Petroleum Institute (API), the New York State Energy Research and Development Authority (NYSERDA) and the California Energy Commission (CEC) initiated a three-year program with GE Energy & Environmental Research Corporation (GE EER). The present work focuses on: (1) Developing valid emission factors and speciation profiles for key categories of stationary sources, especially those found in oil, gas and power industries; (2) designing a new sampler design based on the Hildemann design criteria that increases its applicability to more sources; and (3) establishing a robust standard methodology for fine PM source characterization.

Dilution sampling methods are favored over traditional stack sampling methods for determining chemical speciation of emissions because: a broader range of sampling media and methods can be employed; the same sampling/analysis methods used for chemical speciation of ambient PM can be employed providing directly comparable results; and the conditions experienced by the sample more closely match those experienced by the exhaust gases leaving the stack as they mix with the atmosphere. Many different approaches to dilution sampling are found in the literature. With increasing emphasis on organic fingerprinting, the design established by Hildemann et al. has been adopted in several recent studies. The distinguishing feature of this approach is long residence time (80-90 seconds) to allow condensation and growth of organic aerosols. Pilot-scale combustor tests burning straight and doped natural gas, No. 6 fuel oil, and coal indicate that near-equilibrium aerosol conditions can be achieved at much shorter residence times than previously thought.

Recent field tests have been completed on several full-scale gas-fired sources (1 refinery boiler, 2 refinery process heaters, 1 steam generator, 1 combustion gas turbine) and a refinery fluid catalytic cracking unit. The test results provide improved data for gas-fired sources, where chemically speciated emissions using modern methods were previously not available. While PM emissions from natural gas are extremely low per unit of fuel burned, the large quantities of natural gas currently utilized and the dramatic increase in natural gas use projected over the next 20 years indicate the potential for measurable contribution to ambient PM_{2.5}. Measurement of PM emissions from natural gas-fired sources is especially challenging because of the low concentration. Run-to-run variability is typically large when using traditional stack test methods, such as

U.S. EPA Methods 201A, PRE4 and 202. This high variability is observed, for example, in an examination of 92 source tests on 36 different combustion turbines. The variability is attributed to random non-combustion generated particles (e.g., tube scale or refractory chips) and artifacts in the measurement of condensable particulate due to trace amounts of sulfur in the fuel leading to artifact sulfate formation in the liquid impingers. Also, sulfate and other artifacts result in a large positive bias in the condensable particle measurement using traditional methods. Modifications to the traditional methods found to reduce variability include run times of 4 to 6 hours to increase sample volume; use of an in-stack PM10 cyclone to separate random non-combustion generated particles; purging of the impinger train with nitrogen following sample collection to reduce sulfate artifacts; and modification of the quartz filter assembly to permit weighing of the filters with the filter support and gasket as an integral unit. However, a large positive bias due to accelerated aerosol condensation in the impinger train remains with the traditional methods. Dilution sampling reduces both the variability and positive bias from these artifacts. Chemical speciation of emissions from the large frame gas turbine equipped with oxidation catalyst and selective catalytic NO_x reduction show that carbon accounts for the largest fraction of the fine PM emissions and that traditional methods overestimate both sulfate and mass emissions. These results will be discussed in more detail in the paper.

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